Valorisation of the Argan fruit pulp: a source of latex?

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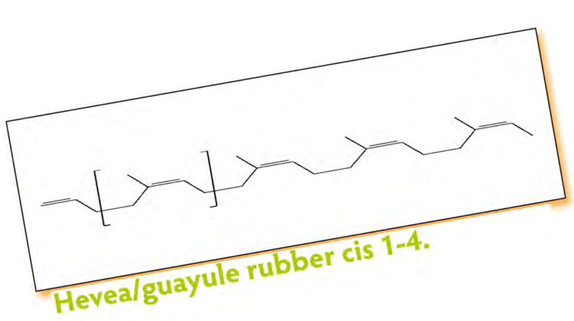
ARGAN TREE (*Argania spinosa*, Sapotacea family), adapted to harsh environment, heat, drought and poor soil, and endemic of South-West Morocco, is a source of forage for goats, of a high-value oil, and of fire-wood. The Argan oil is extracted from the nut, while the pulp contains a latex as do 2.000 species producing natural rubber: polyisoprene having a cis 1-4 (Hevea, *Parthenium argentatum,* Taraxacum Kok Saghyz) or a trans 1-4 stereochemical structure (gutta percha). Battino (1929) was the first to isolate latex from Argan pulp and showed it was a trans-isomer. Sandret (1957) found that this latex contains rubber at a concentration of 0.11 to 0.48% (fresh weight). Fellat-Zarrouck et al, (1987) have shown that this polyisoprene of the Argan pulp can be either of the cis and trans structure, but that cis was prominent. Within the project RARGA PROD 2, CIRAD and Agropolis have studied the valorisation of the Argan pulp, especially the rubber fraction.

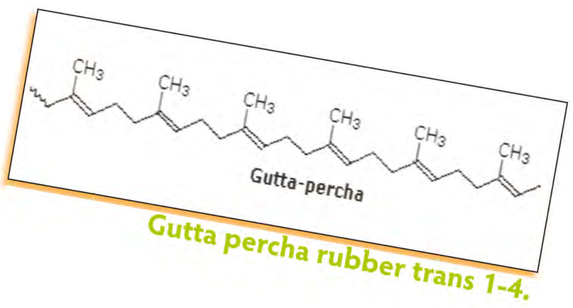
FTIR analysis

- υC=O at 1735-1750 cm^{-1} (fatty acid ester and protein carboxyl groups).
- υC=C at 1620-1690 cm^{-1} (polyisoprene and lipids).
- υC=C at 800 et 840 cm^{-1} (cis polyisoprene).
- υC-H at 2850-3000 cm^{-1} and 1370-1470 cm^{-1}.

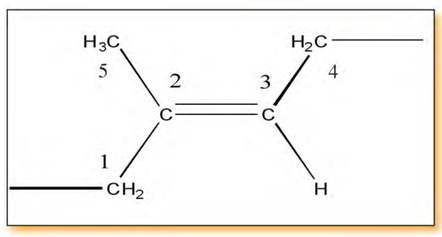
Argan rubber is a polyisoprene.



Hevea/guayule rubber cis 1-4.



Gutta percha rubber trans 1-4.



NMR ^{1}H analysis

- δ CH_3 (C_5) 1.63 ppm for cis 1-4 and δ CH_3 1.53 ppm for trans 1-4 stereo-isomer.
- δ CH_3 (C_5) 0.8-1.0 ppm and CH_2 (C_1 or C_4) 1.2-2.0 ppm and small peaks above 2 ppm belongs to long chains of saturated lipids and not to polyisoprene.
- For pure polyisoprene, total integration of all aliphatic groups below 2.5 ppm should be 7 times the peak at 5.0 ppm of CH (C3) but it varies from 13 to 23 times, this confirms the presence of lipids.

Co-existence of the cis and trans isomers respectively.

Percentage cis and trans isomer in argan crude rubber.

Type of fruit (shape & maturity)	RMN^{1}H	RMN^{1}H	RMN^{13}C	RMN^{13}C
	1-4 cis	1-4 trans	1-4 cis	1-4 trans
Round half ripe	27.5	72.5	25.5	74.5
Sharp ripe	46.5	53.5	46.8	53.2
Round ripe (infected)	48.0	52.0	49.2	50.8
Round unripe	44.1	55.9	42.9	57.1

NMR ^{13}C analysis

- δ CH2 at 23-30 ppm is characteristic of lipid chains (confirmed by FTIR band 1733cm^{-1}).
- δ (C_2) 135 ppm and δ (C_3) at 125 ppm is characteristic of a polyisoprene.
- δ CH_2 32.2 ppm and δ CH_2 (C_1) at 39.8 ppm is a cis and trans respectively.

***Argania spinosa* synthetises the two forms of isomers of polyisoprene cis 1-4 and trans 1-4. Sapotacea species are generally trans.**

Argan rubber DSC analysis.

Type of pulp	Tm °C	Tg °C
Round half ripe	53.9	-54.9
Sharp ripe	56.2	-65.9
Round ripe (infected)	57.8	-63.0
Round unripe	61.0	-65.0
Gutta percha	62.4	-66.9

DSC analysis

- Melting point (TM) between 54-61°C corresponding to a trans 1-4 polyisoprene (gutta percha).
- Glass transition temperature (Tg) between -54°C and -65°C for cis 1-4 polyisoprene.

DSC confirms cis and trans polyisoprenes in Argan rubber.

Molar mass of argan rubber.

Sample	Mw (kg/mol)	Mn (kg/mol)	I	Rg (nm)
M885	58 (1)	52 (1)	1.1	7
M886	128 (20)	97 (8)	1.3	23
M887	143 (20)	46 (2)	3.1	32

( )= standard deviation

SEC-MAL analysis

- Polyisoprène of argan pulp has low molar mass between 58.000 and 143.000 g/mole (fig. 1). The Mw is much lower than hevea rubber (1 to 2,5 x 10^6) or guayule rubber (6 to 9 x 10^5).

The values are more characteristic of a liquid polyisoprene.

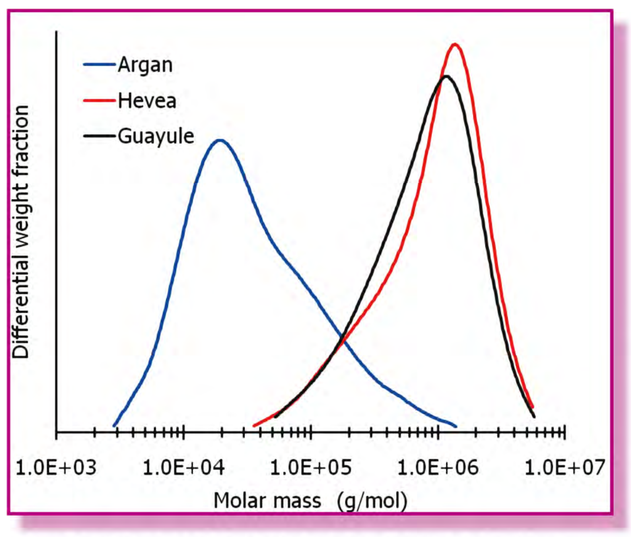


Fig. 1. Molar mass distribution for rubber from Argan, Hevea and Guayule analyzed by size exclusion chromatography coupled to a multi-angular light scattering detector (SEC-MALS).

Conclusion

- The rubber of Argan pulp contains the two polyisoprene isomers, cis 1-4 and trans 1-4, while rubber from Sapotacea sp. (Gutta percha, Balatta) is mainly trans 1-4 polyisoprene, and Asteracea (*Hevea*, Guayule) contains only cis polyisoprene.
- ^{1}H and ^{13}C NMR and FTIR spectra show contamination of rubber extracts by long chains of lipids which explains the high percentage of 1-4 cis C=C bonds, but not from polyisoprene.
- DSC confirms trans isomer.
- The average molar mass (Mw) of Argan rubber is much lower than that of Hevea and Guayule.
- This potential source of rubber should find applications, based on its peculiar composition.

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